CHAPTER - 10
SUMMARY AND CONCLUSIONS

10.1 SUMMARY

The first chapter deals with the general introduction of the nanoscience and nanotechnology and also the classification of nanomaterials based on the quantum confinement. A brief note on the core/shell nanoparticles (CSNPs) and its various types are discussed in detail. The two broad categories of the synthesis of nanomaterials such as Top-down and Bottom-up approach have explained briefly with suitable examples.

A detailed literature survey of the present research topic is reviewed and particularly on the synthesis, structural and properties of the CSNPs are reported. It includes, the recently reported works related to the dielectric and magnetic properties of the CSNPs and described in the second chapter.

The third chapter deals with the scope of the present investigations on magnetic and non-magnetic based CSNPs. The researcher justifies the selection of core and shell part of the CSNPs for the dielectric relaxation and magnetic studies. In these core-shell nanosystems, Fe$_2$O$_3$, NiFe$_2$O$_4$ and NiO have been used as a magnetic part and Gd$_2$O$_3$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (calcium phosphate) have been used as a non-magnetic part. The dielectric relaxation studies were investigated for magnetic NPs (Fe$_2$O$_3$ and NiFe$_2$O$_4$) encapsulated non-magnetic material (Gd$_2$O$_3$). In the case of magnetic studies, CSNPs have been designed as the magnetic shell (NiFe$_2$O$_4$ and NiO) with non-magnetic core (Gd$_2$O$_3$). In addition to this, the thermal stability of magnetic core encapsulated by non-magnetic shell in a core-shell structure was analysed for 650 ºC heat treated samples.
The fourth chapter explained the experimental methods involved in this investigation. The simple and effective methods such as polyol and co-precipitation techniques have been used for the preparation of nanomaterials and discussed. The instruments used for the characterisation of these prepared samples also described.

The fifth chapter deals with the measurement of dielectric relaxation of the Fe$_2$O$_3$/Gd$_2$O$_3$ CSNPs by alternating current impedance spectroscopy. Crystal phase and core-shell morphology of the polyol mediated synthesised samples are confirmed by X-ray diffraction study and TEM respectively. Temperature dependent relaxation times are analysed and mechanism responsible for the conduction or dielectric relaxation in these CSNPs is found from the Arrhenius law. The relaxation mechanism of Fe$_2$O$_3$/Gd$_2$O$_3$ CSNPs has been discussed in the framework of conductivity and permittivity formalisms.

In the sixth chapter, the researcher explored and studied the effect of shell material and core-shell interface on the dielectric properties of core-shell nanosystem of Gd$_2$O$_3$ coated NiFe$_2$O$_4$ NPs. The Nyquist plots of impedance data are analysed by the RC equivalent circuit having a constant phase element. The dielectric relaxation is modelled by Havriliak–Negami technique in the electric modulus formalism. From these investigations, it may be concluded that the crystalline phase of the core material (NiFe$_2$O$_4$) is stabilized by the shell material (Gd$_2$O$_3$).

The seventh chapter deals with the studies on spin relaxation characteristics of Gd$_2$O$_3$/NiFe$_2$O$_4$ CSNPs by EPR spectroscopy. The phase formation and core-shell morphology of the polyol mediated synthesised Gd$_2$O$_3$/NiFe$_2$O$_4$ CSNPs are confirmed by XRD and TEM respectively. The temperature dependent EPR parameters, ΔH$_{pp}$, g$_{eff}$, N$_s$ and T$_2$ are studied in the temperature ranging from 110 K to 300 K. The Gd$_2$O$_3$/NiFe$_2$O$_4$ CSNP shows the minimum loss in the high frequency region.
compared to bare NiFe$_2$O$_4$ and Gd$^{3+}$ doped NiFe$_2$O$_4$ NPs. The room temperature magnetization of these CSNPs was studied by VSM.

The eighth chapter deals with the magnetic and spin-relaxation studies of NiO encapsulated Gd$_2$O$_3$ CSNPs and analysed in the temperature range of 300 K to 110 K by EPR, at a frequency of 9.43 GHz. The phase pure Gd$_2$O$_3$, NiO and Gd$_2$O$_3$/NiO CSNPs are synthesised by polyol process. Core-shell morphology of Gd$_2$O$_3$/NiO CSNPs was analysed by XRD, Raman spectroscopy and TEM. The „$g$” factor, spin relaxation time and number of unpaired spins present in the sample with different temperature are determined by EPR spectra. The significant of anisotropy field and interfacial exchange coupling between the core and shell region for these CSNPs at low temperature have been discussed.

The ninth chapter describes the structural and magnetic studies of hydroxyapatite (HAP) – encapsulated $\gamma$-Fe$_2$O$_3$ CSNPs. Encapsulation of the magnetic NPs with HAP shell material prevents the agglomeration of the magnetic core particles. Single and multi-core core-shell morphology of the particles is confirmed by TEM analysis. It may be concluded from the hysteresis curve and Mossbauer spectrum of $\gamma$-Fe$_2$O$_3$/HAP CSNPs, the coating of HAP over the iron oxide core enhances the thermal stability of $\gamma$-phase Fe$_2$O$_3$ up to 650 °C.
10.2 CONCLUSIONS

In this Ph.D research work, the researcher has synthesised and characterised five types of heterogeneous core-shell nanoparticles (CSNPs) using chemical method and the materials are given below,

(i) Fe₂O₃/Gd₂O₃ CSNPs
(ii) NiFe₂O₄/Gd₂O₃ CSNPs
(iii) Gd₂O₃/NiFe₂O₄ CSNPs
(iv) Gd₂O₃/NiO CSNPs
(v) Fe₂O₃/Ca₁₀(PO₄)₆(OH)₂ CSNPs

In order to obtain nanosized powders of the compound, inexpensive and simple method of chemical synthesis the polyol and co-precipitation methods have been adopted. The structural (XRD), microstructural (SEM and TEM), dielectric, magnetic properties and electron paramagnetic resonance of the prepared CSNPs have been investigated. The main conclusions drawn from the present investigations are the followings,

- XRD analysis of the samples shows the formation of phase pure compounds with different crystal structures at room temperature. In these core-shell heterogeneous nanosystems, the core and shell material has different lattice constant. Due to this lattice mismatch, there is a overlapping of the diffraction peaks for these two materials particularly between the similar diffraction angle position of the core and shell material. Because of this lattice mismatch, shell material experiences the strain during the epitaxial growth on the surface of the core material and it causes a shift in the diffraction peak angle from their original position. In Raman spectroscopic analysis for these CSNPs, the core materials peaks are suppressed due to the mass effect of the shell material.
• The TEM micrographs of the samples confirmed the core-shell morphology of these prepared heterogeneous NPs.

• The dielectric relaxation mechanism for Fe$_2$O$_3$/Gd$_2$O$_3$ CSNPs has been discussed in the framework of conductivity formalisms. The value of the activation energies calculated from impedance, electric modulus and d.c. electrical conductivity those are almost identical and also suggesting a hoping conduction mechanism responsible for the relaxation in the Fe$_2$O$_3$/Gd$_2$O$_3$ CSNPs sample.

• From the dielectric studies of NiFe$_2$O$_4$/Gd$_2$O$_3$ CSNPs, the high value of $\varepsilon'$ at frequencies lower than 1 kHz for these CSNPs is attributed to free charge buildup at the interface between the core and the shell region of these CSNPs.

• The dielectric constant of NiFe$_2$O$_4$/Gd$_2$O$_3$ CSNPs at room temperature is 250 at 100 Hz. Semiconducting to metallic transition behaviour at 358 K in NiFe$_2$O$_4$ is not observed in the present CSNPs system. Because of the shell material coating, the thermal stability of the NiFe$_2$O$_4$ core particle has increased.

• From the EPR studies of Gd$_2$O$_3$/NiFe$_2$O$_4$ and Gd$_2$O$_3$/NiO CSNPs, electron spin relaxation of Gd$_2$O$_3$ core NPs could be changed by encapsulation of nanoscale magnetic shell material. The paramagnetic Gd$_2$O$_3$ NPs having the spin-lattice relaxation ($T_1$) characteristics when it was coated with ferromagnetic nanoscale NiFe$_2$O$_4$ shell, it follows the spin-spin relaxation ($T_2$), whereas antiferromagnetic NiO coated Gd$_2$O$_3$ CSNPs are exhibiting the spin-lattice relaxation ($T_1$).
• The EPR spectrum of both Gd$_2$O$_3$/NiFe$_2$O$_4$ and Gd$_2$O$_3$/NiO at 110 K contains an additional small signal in the higher magnetic field region due to the anisotropy present in the sample induced by the strain from the particles surfaces, which is associated with the large surface area of these CSNPs.

• Compared to the bare NiFe$_2$O$_4$ and Gd$^{3+}$ ion doped NiFe$_2$O$_4$ NPs, Gd$_2$O$_3$/NiFe$_2$O$_4$ CSNPs show the lowest loss at 300 K and it is associated with the more number of rare earth atoms present in these CSNPs than the Gd$^{3+}$ doped NiFe$_2$O$_4$ NPs. This is an important factor for this material can be used in the high frequency microwave device applications.

• Low temperature EPR studies were carried out for the non-magnetic core/shell nanosystems. It has been found that the spins of non-magnetic core surfaces are coupled with the shell materials at the core/shell interfaces. When the external field is applied, the magnetic shells spins are rotating with non-magnetic spins along the field direction resulting generation of additional magnetic moments at the interface region. The generated magnetic moments due to the exchange coupling between the core and shell region modify the overall properties of the CSNPs which is different from their single counterpart.

• From the structural and magnetic studies of γ-Fe$_2$O$_3$/HAP CSNPs, there is a strong interaction between HAP and iron oxide NPs surfaces and the interaction imposed by HAP stabilized the crystal phase of γ-Fe$_2$O$_3$ up to 650 ºC.